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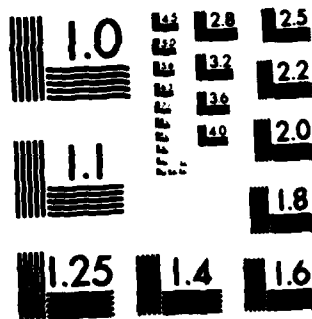
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Experimental and theoretical research efforts on high-energy-density slurry propellants are reported. Transient internal heat conduction and liquid surface regression of a rigid slurry droplet during liquid vaporization and combustion have been investigated using singular perturbation methods. Solutions were obtained depending on the value of ratio of the energy required to raise the interior to the liquid vaporization temperature to that required for liquid vaporization. If this ratio is small, the vaporization time of the core is linearly proportional to both the liquid volume fraction and the square of the overall droplet diameter; if this ratio is large, the vaporization time is approximately proportional to the liquid square of the overall droplet diameter. Experiments on the combustion of JP-10 in suspended slurry droplets were completed, and comparisons with the theory proved successful. Experimentally, a technique to produce isolated slurry fuel droplets of boron and JP-10 has been developed, and observations on the isolated droplet combustion characteristics of several commercially prepared boron/JP-10 slurries were made. Both disruptive burning characteristics and boron particle ignition were found to be functions of the droplet-envelop diffusion-flame temperature and, therefore, the ambient oxygen concentration.

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FUELS COMBUSTION RESEARCH

For the Period 1 March 1982 to 30 September 1985

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SUMMARY

The qualitative mechanisms for the oxidation of benzene and toluene have been greatly improved and show even better correspondence with flow reactor results. The studies of alkylated aromatics have included the propyl benzenes as well. Major results have been obtained on how the sidechain reacts and specific fundamental reaction rate data have been obtained. The fundamental correlation with respect to fuel C-C bonds for the sooting tendency of fuels under premixed combustion conditions has been improved and the concept that fuel structure plays no direct role in determining the critical sooting equivalence ratio was further substantiated by new experimental results for fuel mixtures. Fuel structure and pyrolysis mechanisms have been found to be the important controlling factors in sooting diffusion flames. From a knowledge of basic pyrolysis studies, it is shown that it is now possible to predict a fuel's relative tendency to soot under diffusion controlled mixture. New results with fuel mixtures reveal no synergistic trends with diffusion flame sooting trends; however, these trends may be due to the structural aspects of these flames.

Experimental and theoretical research efforts on high-energy-density slurry propellants is reported. Transient internal heat conduction and liquid surface regression of a rigid slurry droplet during liquid vaporization and combustion have been investigated using singular perturbation methods. Solutions were obtained depending on the value of ratio of the energy required to raise the interior to the liquid vaporization temperature to that required for liquid vaporization. If this ratio is small, the vaporization time of the core is linearly proportional to both the liquid volume fraction and the square of the overall droplet diameter; if this ratio is large, the vaporization time is approximately proportional to the liquid volume fraction raised to an exponent less than unity and the square of the overall droplet diameter. Experiments on the combustion of JP-10 in suspended slurry droplets have been completed, and comparisons with the theory proved successful. Also, experimentally, a technique to produce isolated slurry fuel droplets of boron and JP-10 has been developed, and observations on the isolated droplet combustion characteristics of several commercially prepared boron/JP-10 slurries have been made. Both disruptive burning characteristics and boron particle ignition were found to be functions of the droplet-envelope diffusion-flame temperature and, therefore, the ambient oxygen concentration.

I. PROGRAM OBJECTIVE

General

Interest in improving performance/emission characteristics of propulsion systems requires better understanding of the coupling between fluid mechanical and chemical kinetic processes which occur in these devices. Modelling of the necessary combustion chemistry is impeded by the lack of adequate knowledge as to the general and detailed features of the kinetic mechanisms. More recently, uncertainties in the future sources and characteristics of fuels have emphasized the need to better understand fuel effects on combustion, e.g. energy release distribution, soot formation, emissions, etc. Such information is particularly lacking for aromatic species which now are comprising a major fraction of present fuels and could be a dominant factor in future jet propulsion fuels. Evidence for inferior life times for gas turbine combustor cans now exist and can be related to fuel changes. Recent interest in high performance, high energy density fuels and propellants such as boron- and carbon JP-10 slurries has made it evident that the combustion characteristics of these materials must be understood before the full potential of such fuels can be realized. Thus, currently the research endeavors at Princeton reported here include pyrolysis and oxidation of aliphatic hydrocarbons, pyrolysis and oxidation of aromatics, mechanistic studies of soot formation/destruction, and the vaporization/combustion of high energy density slurries, particularly those containing boron.

The specific objectives of the effort have been:

1. To continue quantitative studies on the pyrolysis and oxidation of aromatics. New results have been obtained for ethyl benzene, the propyl benzenes and styrene and additional results on toluene. Improved general mechanisms have been proposed.
2. To continue studies of the pyrolysis and oxidation reactions of the important aliphatic hydrocarbons known to be intermediates in aromatic oxidation and soot formation. A butadiene study was completed.
3. To study soot formation and destruction processes in premixed and diffusion limited combustion systems. New extensive experiments, particularly dealing with fuel mixtures, have further substantiated the importance of fuel temperature and flame structure as the major controlling parameters in soot formation in diffusion flames and the number of carbon-carbon bonds in the fuel as the controlling factor in premixed flames.

4. To continue experimental and theoretical efforts on elucidating the isolated droplet vaporization/combustion characteristics of boron slurry fuels. Theoretical studies on the vaporization of slurry droplets using perturbation methods have achieved new insights and, the first results on the combustion of isolated burning free droplets of boron/JP-10 slurry fuels have been made in a high-temperature oxidizing environment under conditions of low Reynold's number.

II. STATUS OF RESEARCH

A. Introduction

The following principal tasks are discussed in subsequent sections:

1. aromatic pyrolysis and oxidation
2. aliphatic hydrocarbon pyrolysis kinetics in the presence of various oxygen concentrations
3. soot formation and destruction mechanisms
4. high energy density boron slurry vaporization/combustion properties.

B. The Oxidation and Pyrolysis of Aromatic Hydrocarbons

The initial approach on this aspect of the fuels research program was to challenge what most thought to be a more complex area of chemical kinetics, that is, the oxidation process of the aromatic hydrocarbons. The approach used was to survey and analyze the literature in order to guide the experimentation. The motivation was that again the unique characteristics of the Princeton turbulent flow reactor would permit insights into a complex system. This flow reactor shown in Figure 1 has been described in detail in various publications [1,2,3]. Most of the very early published work on aromatics was performed at low temperatures, nevertheless, proceeding to higher temperatures closer to combustion process levels was thought of as possibly clarifying the mechanism. High temperature mechanisms were needed. Analysis and review of the low temperature work created enough outside interests to warrant publication [4]. This review led to the questioning of the applicability at the higher temperature of the earlier mechanisms proposed.

Specifically, the objectives of this aspect of the program have been to elucidate the mechanisms of the oxidation of aromatic fuels with a particular emphasis on those aspects of the mechanisms which lead to soot and other pollutant formation, and to develop, where possible specific chemical kinetic data on

the individual reactions which make up the complex reaction history of the aromatic hydrocarbons. These results would then permit the development of overall rate expressions for combustor modellers, as had been so successfully done for the alkyl hydrocarbons [5].

As detailed below, great progress [6,10] was made during the contract period. This success is thought to be due in large part to the successful development and operations of the flow reactor; the use of a unique high temperature sampling system; and an automated gas chromatographic apparatus, and the presence of the gas chromatographic/mass spectrographic apparatus purchased under the program.

One key to understanding the oxidation of aromatic hydrocarbons was thought to be the determination of the reaction sequence which consumes the phenyl radical. Extensive data from the oxidation of benzene had been published with a proposed mechanism that revolves around the oxidation of the phenyl radical [6]. Determination of the processes which remove the sidechain from alkylated aromatics and produce phenyl radicals is also critical to understanding the oxidation of aromatic hydrocarbons. Earlier work in this program had produced extensive data and proposed mechanisms for the process of sidechain removal in the oxidation of toluene and ethylbenzene [6,7,8,9]. In these studies a clear analogy between the reactions of the alkylated aromatics and those of the corresponding alkanes was observed [7,8,9]. This analogy strongly suggested that styrene could be the major product of fuel consumption in the normal alkylated aromatic hydrocarbons [9].

During this contract period, the experimental effort has concentrated mainly on the oxidation of normal and isopropylbenzene. The experiments were aimed at testing this analogy to the alkanes and, in particular, the idea that styrene could be the major product of fuel consumption. For the first time in the study of aromatics, experimental results have been successfully used, as well, to obtain kinetic rate constant data on specific reactions of aromatic fuel. Also, the previous ethylbenzene oxidation data have been analyzed under consideration of a steady state of radical species concentrations, and the results of this analysis allow additional kinetic parameters to be derived from the experimental data. Finally, a preliminary test on the oxidation of styrene was performed because uncertainties exist about the reactions which consume styrene, a major intermediate in the oxidation of ethylbenzene and the propylbenzenes. This section will only summarize these new accomplishments.

Experimental results from the oxidation of normal propylbenzene are presented in Figure 2. If the selectivity for benzylic hydrogen (the hydrogen attached to the carbon atoms next to the benzene ring) abstraction were very large, the only product

would be styrene. The styrene would be produced by abstraction of a benzylic hydrogen followed by the loss of a methyl group. Indeed, the results show that styrene is an important product for this fuel; however, it is not the only major one. Therefore, these results do not indicate that benzylic hydrogen abstraction dominates the abstraction from the alkyl group. In fact the presence of toluene and benzaldehyde, early in the reaction strongly suggest that benzyl radicals are present. The most likely route to the benzyl radicals is the abstraction of a primary hydrogen from the sidechain, followed by loss of ethylene. The important conclusion to be drawn from these results with respect to the analogy is that the abstraction of all hydrogens in the sidechain must be occurring, not simply benzylic hydrogens.

Based on the experience with *n*-propylbenzene, the analogy to the early reactions of propane was used to predict the major stable products that would be found in the oxidation of isopropylbenzene. Because the sidechain of isopropylbenzene contains only benzylic and primary hydrogens, only two products are expected to result from radical attack on the sidechain. The loss of a primary hydrogen should produce styrene and the abstraction of a benzylic hydrogen will yield methylstyrene. In fact, the experimental results of Figure 3 confirm these predictions. Thus, the analogy to alkanes successfully predicted the products of fuel consumption, and the ability to make qualitative predictions based on the analogy is confirmed.

In view of the simplicity of the experimental results for isopropylbenzene, an attempt was made to obtain the branching ratio for the production of styrene and methylstyrene. This ratio also represents the selectivity for benzylic hydrogen abstraction compared to primary hydrogen abstraction, and such kinetic information is critical to the eventual modelling of the oxidation of these aromatic fuels. Because the conditions chosen for these experiments ensure that consumption of intermediates is small compared to their production, the slopes of the two product concentrations are a good approximation to their rate of production. Thus, the ratio of the slopes of methylstyrene and styrene gives an overall selectivity for benzylic versus primary hydrogen abstraction. When the ratio is multiplied by six to eliminate the effect of the greater number of primary hydrogens, the selectivity for benzylic versus primary abstraction is 3.5 to 1 in favor of the benzylic [10,11]. This selectivity represents the first result of its kind for aromatics undergoing oxidation.

Additional kinetic parameters have been derived from the analysis of the ethylbenzene results. The path to this accomplishment began with the closer scrutiny of the apparent first order disappearance of the fuel. Because radical attack is the primary path for fuel consumption, the rate equation for the

fuel is simply

$$dF/dt = -k [X] [F]$$

where X is any radical or atom. Figure 4 illustrates the first order loss of the fuel for a lean ethylbenzene oxidation and also shows the value of $k[X]$ derived from the data. Because the experiment was nearly isothermal, the constant value of $k[X]$ implies that the concentration of the radicals is approximately constant. Given this apparent steady state concentration of radicals, the ethylbenzene mechanism was subjected to a steady state analysis, and the resulting differential equations were used in a linear regression analysis of the experimental data. This regression analysis produced values for the rates of production and consumption of styrene in the ethylbenzene oxidation. This technique has been applied to the other experimental results for ethylbenzene and has produced consistent results (see [12]).

The final accomplishment to be summarized is the successful completion of a styrene oxidation test which presented earlier experimental difficulties due to polymerization of styrene in the evaporator system. The results help to clarify the reactions of styrene which is a major intermediate for ethylbenzene and the propylbenzenes. Previously, hydrogen displacement to produce benzene and a vinyl radical was proposed as the major consumption reaction of styrene in the ethylbenzene oxidations [6,9]. In addition, the toluene and benzaldehyde were hypothesized to result from reactions of benzyl radicals produced by homolysis of ethylbenzene [6]. However, oxidation of styrene could also produce these same products. The simplest means to clarify the importance of displacement and oxidation reactions of styrene was to perform a styrene experiment because no alternate routes to toluene and benzaldehyde would be present. The results of this experiment in Figure 5 show large amounts of toluene and benzaldehyde in addition to benzene and clearly indicate that the oxidative reaction is important. This result indicates that the overall modelling of the alkylated aromatics will be somewhat more difficult than initially anticipated, but all results in the program show that major mechanistic trends do exist.

C. Pyrolysis and Oxidation of Aliphatic Hydrocarbons

Because of the non-availability of a graduate student, the work on butane pyrolysis originally proposed was not initiated. Earlier data from this aspect of the program have been reported in the literature [13-16].

D. Soot Formation and Destruction Processes

1. Introduction

The major objectives of Princeton's soot studies have been:

a. a complete and critical review of the soot literature in order to evolve phenomenological models and understanding of the overall processes so that control strategies could be developed.

b. experimental investigations with gaseous fuel jets (laminar diffusion flames) in order to evaluate the effects of water and other additives on the soot formation process and to scrutinize the models developed.

c. experimental investigations with premixed laminar flames for the same purposes of (b).

d. The development of a rapid experimental test to permit evaluation of the sooting tendency of practical liquid fuels, particularly those containing fractions or aromatics.

Items (a) and (d) were completed and are reported as part of five major publications [17-22]. The phenomenological models and the results obtained under Items (b) and (c) have given substantial understanding of soot processes, much of which has practical application. Indeed, this A.F.O.S.R. work has had substantial influence on the direction and thinking of many investigators in the soot field.

2. Research Progress

a. General Background

The review and phenomenological models developed have been published as an A.F.O.S.R. report [17]. The extensive information reported will not be repeated, but the major conceptual ideas promulgated will be reviewed.

The complete soot mechanism in a combustion system is truly very complex. The process may be described in a cursory fashion as follows. Whether starting in a premixed or diffusion flame system, a fuel undergoes pyrolysis and eventually forms a species which is the precursor to the actual soot nucleation process. The precursor then reacts or polymerizes in some manner so that soot nuclei form. During this process, it is feasible that some of the precursors (or even the species forming the precursors) can be oxidized. Nuclei which form can absorb other high molecular weight hydrocarbons which exist in the combustion system. Since the particles exist in high temperature regions, they can

undergo condensed phase reactions which can reduce their hydrogen content and eventually give the highly complex aromatic structure we know as soot. The soot particles can conglomerate and agglomerate while these processes are proceeding. Simultaneously, there can also be oxidation of the particles.

Although the overall soot formation process as defined above seems very complex, this research has been governed by the essential idea that the controlling factors in most sooting combustion systems are the rate of formation of the precursors and the rate of oxidation of the formed particles.

Most investigators have been concentrating their efforts on the nucleation process. Although nucleation is obviously an important step, recent results at Princeton seem to confirm that it is not the controlling one. Nevertheless, the initial review focused on this question and it was considerations which grew out of this study that guided much of our original experimentation on sooting diffusion flames.

The two primary soot formation mechanisms that have been suggested in the past have been the polyacetylene route and ion-neutral route. Doubts have been raised about the polyacetylene route because it is known that in flame processes soot forms very early. The time required for the numerous free radical-neutral acetylene reactions, the energy required for cyclization, etc. have led us and others to question this type of mechanism. There is substantial evidence that polyacetylenes form in flames, but their fate may simply be to be destroyed or absorbed on particles already formed. The concept of fast ion-neutral reactions being the nucleation route is also open to serious question. Firstly, there are much smaller ion concentrations in diffusion flames than in premixed flames, yet the propensity to soot in diffusion flames is far greater than in premixed flames. More importantly, the ion concentrations in flames are orders of magnitudes lower than the formed particle density. Thus, it would appear that there simply is not sufficient ions present to nucleate all particles.

A suggestion of Thomas [23] that Diels-Alder (condensation) type reactions were fast and a possible nucleation route for soot formation directed the original Princeton conceptions. The thinking followed the lines that any soot precursor must be highly conjugated to be stable at the high temperatures in flames, and, indeed the high molecular weight species forming from these precursors must be conjugated as well. Conceptually then, one could understand why the aromatics had a strong tendency to soot. In a very classical sense, Diels-Alder reactions are very much like electrostatic reactions and if one examines the resonance structures of most compounds which undergo Diels-Alder reaction, one can understand from the polar nature of some of these structures the possibilities of these

reactions. If this conceptual idea were correct, then certain compounds such as butadiene and vinyl acetylene should have a great propensity to soot. Indeed, Schalla, et al. [24] reported that butadiene had a greater tendency to soot than the aromatics. Early experimental work at Princeton, however, had shown butadiene to be a prolific sooter, but contrary to its position with respect to other fuels as Schalla had found. However, recent results [25] with purified butadiene now make our results with this important fuel more consistent with others. The evidence obtained supports the contention that vinyl acetylene and butadiene or their radicals may be the main precursors to soot nucleation. The fact that vinyl acetylene undergoes Diels-Alder addition to form the aromatic molecule styrene lead to the belief that it is the more important of the two precursors. Indeed, the importance of the kinetic studies on the oxidation of aromatics, reported earlier [6.7], is now most evident. The fact that vinyl acetylene and butadiene form in the oxidation of aromatics may be the key to understanding soot formation processes in an aromatic-fuel, premixed combustion system. However, recent estimates of the pre-exponential A factor in the rate expression indicate that simple Diels-Alder reactions may be too slow for the soot forming process. The possibility was suggested that the butadienyl radical could readily become ionized whereby its dissociation products would also be so, and very fast Diels-Alder reactions could proceed. It is interesting that recently Frenklach, et al. [26a] have proposed a soot formation mechanism for alkyl compounds in which the formation of the butadienyl radical is a key controlling step.

Most of the early work on soot formation in premixed flames (Street and Thomas [27]) compared the relative tendency of fuels to soot and reported the tendency as:

aromatics > alcohols > paraffins > olefins > acetylenes.

It was observed that except for the aromatics, the trend was not just a matter of a homologous series trend or the C/H ratio, but the greater the flame temperature the less the tendency to soot. This conclusion was consistent with what Milliken [28] had reported from his considerations of premixed ethylene-air flames that the tendency to soot was a function of the flame temperature. Milliken calculated that the rate of "pyrolysis" of acetylene to form the soot precursors rose more slowly with temperature than the rate of oxidative attack on the precursor forming system. Thus under premixed conditions, the only reason that acetylene seems to have little tendency to soot compared to other fuels is its high flame temperature compared to the other alkyls. Since our work on the oxidation kinetics of alkyls indicated that under rich conditions all compounds break down to acetylene, it was postulated that to a first order the sooting tendency of the alkyl compounds under premixed conditions are independent of fuel structure and primarily a function of the

temperature of the combustion system. It was this conceptual idea that guided the experimental work on premixed flames to be discussed subsequently.

The question of how the aromatics behave with respect to sooting is apparently a different one. Benzene, for example, has a temperature close to ethene, yet, its tendency to soot is greater. From the initial review of aromatic oxidation [4], the conclusion was that the mechanism was such that carboxyl structures formed and these led to radicals which eventually formed CO_2 directly. Thus, the demands for two carbon atoms in the ring was for two oxygen atoms each compared to the fact that all alkyl compounds eventually take a route through a formyl group and only form CO . Thus, it was stated that benzene at a given equivalence ratio was richer than an alkyl compound of the same C/H ratio. This condition was thought to give the great tendency of benzene to soot and not to have correspondence with respect to the temperature trend of the alkyl compounds. Again, the belief that experimental results on the oxidation of the aromatics has helped clarify this point. The results show that it is not likely such carboxyl structures will form during the oxidation of the aromatics, certainly not at the high temperatures of combustion systems. However, the analyses also show that vinyl acetylene and butadiene form as well as acetylene. An extension of this concept is that acetylene must form such compounds to undergo soot nucleation steps. Milliken's concept was that acetylene pyrolysis to soot versus rate of oxidative attack determined the trend to soot with respect to temperature. His concept apparently holds for all alkyl compounds because they follow the same degradation route to acetylene. The aromatics do not follow this route. Instead, they go directly to important soot precursors. Thus, the competitive trend with respect to precursor formation and oxidative attack can be altered substantially.

The reasoning of the temperature effect under premixed conditions can be extended, quite simply, to diffusion flame systems in order to determine the temperature effect. Since there is no oxidative attack on the soot precursor process in diffusion flames, then the pyrolysis rate increase with temperature is not counteracted by any other effect. Thus, the higher the fuel stoichiometric flame temperature the greater the tendency to soot. The general tendency as reported by Schalla et al. [24] long ago shows the trend according to homologous series:

aromatic > acetylenes > olefins > paraffins > alcohols

Again, except for the aromatics, the trend is the greater the stoichiometric flame temperature the greater the tendency to soot. However, Schalla, et al. results show that the C_4 olefins had the greater tendency to soot among the olefins. Further,

branched chain isomers had a greater tendency to soot than the corresponding straight chain compounds. The characteristic of benzene pyrolysis would have to be different from the alkanes. These facts led to the conclusion that the tendency to soot in diffusion-controlled systems was dominated by the stoichiometric flame temperature and the fuel structure. Indeed, this concept guided much of the experimentation with the fuel jet diffusion flames to be discussed next.

b. Sooting Tendency in Diffusion Flames

In earlier work it had been shown that addition of an inert did not alter the luminous flame height of a diffusion-controlled system [18]. Thus, by the addition of an inert to the gasified fuel the temperature of the diffusion flame could be controlled independently. The actual measurements proceed by measuring the smoke heights (and the mass flow rate at this height) with various amounts of a nitrogen diluent. Since the model of soot formation was that fuel pyrolysis kinetics control, the data were plotted as the $\log (1/\text{fuel mass flow rate (FFM)})$ vs. $1/T$ and it was found that straight lines were obtained for all fuels tested. In major publications [18,29], extensive results were presented on many compounds such as acetylene, ethene, butane, propene, n-butene, pentene, hexane, etc. and the effect of ambient oxygen concentrations.

In previous years data on the xylenes, ethylbenzene, 1,3 and 1,4 cyclohexadiene, C3, C4, and C5 cycloalkanes, C5 and C6 cycloolefins, 1-methylnaphthalene and purified 1,3 butadiene were reported. During the subject period, data on the following pure fuels: neopentane, n- and iso-octane, iso-butane, decalin, tetraline, 1-methylnaphthalene, 1,3 and 1,4 hexadiene and allene have been obtained. The work also was extended to fuel mixtures and extensive measurements for various benzene/1-hexene mixtures have been obtained.

The benzene/1-hexene mixture data are reported in a recent publication (30) as are the pure fuel data (14). Figure 7 shows a plot of $\ln(1/\text{FFM})$ vs. $1/T$ for these data and Figure 8 shows some of the basic data reported previously. In choosing the pure fuels, consideration was given to effects of the "compactness" and the degree of resonance stability of the fuel molecule. As previously concluded, the essential characteristic found was that in diffusion flames, two factors control the extent of soot formation, namely the flame temperature and the fuel pyrolysis kinetics. By fuel pyrolysis, it is meant that both the rate of pyrolysis and the nature of the unsaturated intermediate hydrocarbon species which form are important. For each fuel tested, the location on the $\ln(1/\text{FFM})$ vs. $1/T$ plot can be explained from consideration of pyrolysis data reported in the literature. In addition, the trends found are precisely those found by Frenklach et al. [31] who measured soot yields in shock tube pyrolyses of

many of the pure fuels tested. This agreement is significant because the physical situation behind a shock wave is drastically different from that in a flame, yet the trends are the same. This correspondence indicates that the results are not peculiar to the experimental techniques reported here. The powerful conclusion to be made is that the relative sooting tendency of a given fuel in a non-premixed environment can be determined given a knowledge of its pyrolysis kinetics.

The fuel mixtures were tested with the usual temperature control by N₂ dilution in order to determine if any chemical synergistic effect takes place. The benzene/1-hexene mixtures were chosen as the most widely studied combination because these components are representative of the aromatic and olefinic classes which have vastly different sooting tendencies and because this mixture of two liquid fuels is easily implemented in the laboratory apparatus. In agreement with the work of Gill et al. [32], it was found that no synergistic effects take place in the flames. In other words, each fuel component forms soot independently of the other components so that presently it would appear that the sooting tendency of a mixture can be predicted given the sooting tendencies of each component burning as a pure fuel. In fact, the relative contribution to the total soot loading from each component can be estimated by normalizing its actual mass flow rate in the mixture to its mass flow rate at the smoke point when burned as a pure fuel at the same flame temperature. This normalization must be borne in mind as it demonstrates that the more highly sooting fuel component will contribute a fraction of soot loading which is greater than its fraction as a fuel component. For instance, in a 15 mole% benzene-85 mole% hexene flame, each component will provide a roughly equal contribution to the actual soot loading. The manner in which these mixture results are correlating, that is that there is no synergism between any fuel combination, may be due to the structure of the diffusion flame in the smoke height tests used here and by other investigators. It is well established that soot forms on the fuel rich side of the diffusion flame. But one must remember that there is a steep temperature gradient from the diffusion flame front to the center line of the cool fuel jet. Thus, a given fuel in a mixture may pyrolyze and form before the other fuel's pyrolysis steps have been initiated. Thus, the possibility that the pyrolysis radicals of one fuel may facilitate the formation of soot by adding to the pyrolysis products of another fuel may not exist due to spatial separation caused by the temperature effect on the pyrolysis of the two fuels in the combination. Under a new AFOSR contract, ideas are being explored on how to overcome this structure dilemma.

To summarize, the smoke point results of Figures 7 and 8, show that 1-methylnaphthalene has the greatest tendency to soot with a mild dependence on temperature. All aromatics have relatively the same tendency to soot and also have a mild

temperature dependency. The diolefin, butadiene, is the next greatest sooting fuel and is followed by the olefins and those fuels which pyrolyze to the olefins. All olefins have a much greater temperature dependency. Then come acetylene and the paraffins. As would be expected, acetylenes have a very large temperature dependency. Application of these type of results to practical power plants has been discussed in a AFOSR technical report.

c. Sooting Tendency in Premixed Flames

The qualitative procedure for evaluating sooting tendency of fuels under premixed combustion conditions has been to observe the C/O ratio (or equivalence ratio ϕ) at which luminosity just begins in laminar Bunsen type flames. The larger the C/O or equivalence ratio at which luminosity begins, the less the tendency to soot. The most extensively published data of this type have been those of Street and Thomas [27]. Milliken's interpretation [28] of the competing phenomena in premixed flames made it evident that the C/O ratio was not necessarily the primary variable for categorizing fuels with respect to their tendency to soot under premixed conditions. Indeed, from oxidation kinetics one would expect acetylene to soot the most, not the least, among the alkyls. Thus, experiments of the Street and Thomas type were repeated with temperature control of the flame at each mixture ratio. The control was achieved by varying the nitrogen concentration in a nitrogen-oxygen mixture. Thus for a given fuel, a temperature higher or lower than the value for air could be obtained.

An interesting experimental procedure developed permitted very fuel-rich operations with great dilution without stability or cellular flame problems [33]. Essentially, the Bunsen cone stabilization point was carefully enriched with air. Further, it was also found that the data taken on many fuels gave the most meaningful trends (i.e. with what one knows with respect to fuel pyrolysis kinetics) when plotted as the equivalence ratio (ϕ) based on stoichiometry going to carbon monoxide and water vapor versus the calculated adiabatic flame temperature [33]. The fuels considered at that time were: 2-methyl propane and 1,3-butadiene. Work was completed recently on: hexane, 1-hexene, cyclohexane, cyclohexene, 1-octene, benzene, toluene, cumene and 1-methyl naphthalene. The critical sooting equivalence ratio ϕ_c for all these data are plotted in Figure 9.

Due to a model developed which correlates the sooting tendency of all fuels tested in these programs, it is believed that sooting tendencies with premixed combustion conditions is completely understood.

The reasoning [34,35] is as follows. Since the pyrolysis and oxidation rates follow Arrhenius kinetics, then a plot of

$\log \psi_c$ versus $(1/T_f)$ should produce a straight line for each fuel. Figure 10 shows that the data explicitly correlate in this manner over the entire temperature range investigated experimentally. The natural tendency is to assume that the Arrhenius plot represents an activation energy of some controlling process in the system. Under premixed conditions, however, the inference made is that the balance between the fuel pyrolysis rate and the oxidative attack on the precursors is the controlling factor in determining the sooting tendency. Both the pyrolysis and oxidation attack follow Arrhenius kinetics and thus, this method of plotting should give straight lines for the data. One should notice that the slope of each fuel line is almost identical. The apparent activation energies determined from Figure 10 are within the range of 3-6 kcal/mol for all fuels examined.

In order to understand the effects of the flame temperature, the number of carbon atoms, the C/H ratio, and the fuel structure, an overall analysis of the soot formation process was found to be useful. Milliken's [28] formulation of the problem may be modified by considering the initial fuel generally instead of acetylene explicitly. Consequently, the rate of soot precursor formation may be taken as zero at the critical mixture ratio at which soot just appears; i.e.,

$$(dS_p/dt) = k_p [\text{Fuel}] - k_o [\text{OH}] [P]_c = 0. \quad (1)$$

where $[P]_c$ is the critical concentration of precursors that gives soot. By using Arrhenius parameters, the OH concentration then may be written as

$$\begin{aligned} \log [\text{OH}]_c &= [(E_o - E_p)/2.3 RT] + \log (A_p/A_o) \\ &+ \log [\text{Fuel}]_c \end{aligned} \quad (2)$$

where the subscript c expresses the critical condition. The equilibrium OH concentration may be utilized in order to observe the differences due to fuel type. The equilibrium OH concentration may be written as

$$\log [\text{OH}]_{eq} = a(1/T) + b + c \log \psi. \quad (3)$$

The fuel concentration in the mixture is an approximately linear function of ψ in the range of the fuel mole fraction less than 0.1. Then, at the critical conditions,

$$[\text{Fuel}]_c = d \psi_c. \quad (4)$$

By substituting Eqs. (3) and (4) into Eq. (2) for the critical condition, and finds that

$$(1-c) \log \psi_c = - [(E_o - E_p)/2.3 RT] + a (1/T) +$$

$$b + \log (A_p/A_o) - \log d + \log [P]_c \quad (5)$$

or

$$\log \psi_c = \left[\{ (E_o - E_p)/2.3 R + a \} / (1-c) \right] (1/T) + C, \quad (6)$$

where C contains all terms independent of T.

Thus, the temperature effect on the sooting limit may be evaluated, in an overall sense, in terms of the activation energies of the fuel pyrolysis (E_p) and the precursor oxidation process (E_o) and the dependencies of the OH radical concentration on the flame temperatures (a) and the effective equivalence ratio (c). Fuel pyrolysis studies [13] have revealed that the overall activation energies of pure pyrolyses are approximately the same (65 kcal/mol) for six aliphatic fuels (propane, butane, isobutane, 1-butene, hexane, and 1-hexene). The activation energies for the OH radical attack on the soot precursors also do not vary greatly with initial fuel type and must be very small, probably 0-7 kcal/mol. The equilibrium OH concentration for several fuel/oxygen/nitrogen mixtures at $\psi = 1$ was calculated. The most significant feature as would be expected, is that the slope of each fuel OH line as a function of $(1/T)$ is identical for all fuels ($a = -1.6 \times 10^4$). The apparent "activation energy" determined from the slope is 74 kcal/mol. The coefficient c is about -2.5 for all fuels in Figure 10 except for benzene (-3.1) and acetylene (-3.3). Thus, almost all factors which determine the temperature effect on the sooting tendency are minimally related to the fuel type. The sum of the apparent "activation energy" of the OH radical concentration and the activation energy of the precursor oxidation process as calculated is somewhat larger than the estimated activation energy of the fuel pyrolysis process. The arguments made would dictate that the difference in these two values should not change with the fuel type. It is rather remarkable that the experimental data as correlated in Figure 10 not only reveal this fact, but also show a slope (3 - 6 kcal/mole) that is almost the same as that estimated (1 - 3 kcal/mol) from Equation (6).

The coefficient b or the OH concentration at a fixed T_r and ψ , decreases monotonically with increasing C/H ratio and does not depend on either the number of fuel carbon atoms or the structure. Thus, increasing the C/H ratio at a given number of carbon atoms reduces the oxidation rate and increases the tendency to soot. On the other hand, for a homologous series the overall reaction rate constant for pure pyrolysis at a fixed temperature (or A_p) increases dramatically with increasing number of carbon atoms [13]. The coefficient d decreases with

increasing carbon number, but this effect would be less important as compared with the pyrolysis rate effect. Therefore, the increase in the sooting tendency with increased number of the carbon atoms can be explained by the increase in the fuel pyrolysis rate.

Figure 11 shows the heuristic correlation between the critical effect equivalence ratio to soot (ψ_c) at a fixed flame temperature (2200 K) and the "number of C-C bonds" in which a double bond is counted as two and a triple bond as three. The total C-C bond strength which almost linearly depends on the "number of C-C bonds" can be used as well [33]. All data, even those for the aromatics, lie on a single curve. Thus, it appears possible to categorize fuels with respect to their degree of sooting under premixed conditions by use of a single property of the fuel, the "number of C-C bonds" or the total C-C bond strength. This correlation has further significance [33] in that it reveals that aromatic structure is not significant under premixed sooting conditions and led to the proposal that in this type of combustion system all fuels break down to elemental species which then build up to the precursors. Obviously, molecular size has an effect. During this subject period, this model has been improved upon even further [36], but the crucial trends as described above remain the same.

The important physical significance of the correlation is that in premixed combustion systems all fuels must break down to the same common elements which then build to form the soot particles; i.e., fuel structure per se plays no role in determining the critical sooting equivalence ratio ψ_c . (It is obvious that if one formulates a mixture much richer than ψ_c , then the process takes on diffusion flame characteristics and as stated in the previous section, fuel structure will play a role). To verify this concept of no fuel structure role in determining our correlations, during the subject period experiments were performed with mixtures of fuels and using the same temperature control techniques. The fuel mixtures chosen were ethene/octene and benzene/acetylene - two notably different combinations. In the ethene/octene combinations average number of C-C bonds can be created that are equivalent to propene, butene and hexene. Figure 12 reveals that the combinations give the same results as the respective pure components. Also plotted on Figure 12 is the acetylene/benzene results. Although for the mixture combination chosen, there is no pure fuel with an equivalent number of C-C bonds, the experimental results agree perfectly with the correlation for all other pure fuel combinations. These results were recently reported [36]. It is concluded that the postulate that fuel structure plays no role in determining the critical sooting equivalence in premixed combustion systems has been substantiated. The recent work of Harris and Weiner [37], that acetylene controls the mass of soot formed in premixed flames would appear to agree with the postulate and indicate that

acetylene is the major common element to which the initial fuel breaks down under rich conditions to form soot.

E. High Energy Density (Boron Slurry Vaporization/Combustion Processes)

1. Introduction

Efforts on metal and slurry combustion progressed substantially during the contract period. Early work under this effort on boron particle combustion [38] helped to identify critical areas of unknowns that impair assessing the utility of boron as a fuel in propulsion applications. A recent workshop [39] in which the investigators participated served to further define key questions still outstanding in boron combustion. It is especially noteworthy that recent work at Princeton on boron slurry droplet combustion [39-48] forces some revision in certain workshop conclusions--specifically those concerning agglomeration of slurry droplets. For example, disruption rather than agglomeration of slurry droplet appears to be the rule [42] and calculated temperature profiles in the liquid [40,41,47] show substantial temperature variations that could be consistent with various disruption mechanisms. These new findings need improved quantification and analysis to ascertain details of mechanisms, but even in the absence of thorough understanding, they tend to revise the focus of the key problems. If disruption and ignition are rapid, then what can be the cause of long burning times in practical devices? That the chemical kinetics of combustion of fine particles is the most likely further critical area can be inferred rather clearly [38].

Research on slurries was directed toward obtaining a fundamental understanding of mechanisms of vaporization/combustion for slurry droplets. This undertaking was achieved through combined experimental and theoretical studies and is needed to provide direction for investigation of useful modifications to combustion systems and fuel formulations to improve the performance of slurry-fueled propulsion devices.

2. Theoretical Work

In the theoretical work on slurry-droplet combustion, the objective has been to define and analyze simplified models of the combustion of slurry droplets to provide predictions of the parametric dependencies of burning properties on fuel properties and experimental conditions. The important burning properties are not only the burning time and regression history, but also temperature-profile histories within the droplet during burning, for later use in analyses of disruption. A model suitable for these purposes has now been identified, and its analysis by asymptotic methods has been completed [47].

In this work the transient internal processes of heat conduction and liquid surface regression are investigated theoretically. In one analysis [40], the volume fraction of solid particles is considered large enough so that the overall droplet diameter is constant while in another [44], applicable at smaller volume fractions, the overall diameter decreases with time. At the higher volume fractions, vaporization occurs at the regressing surface of an inner sphere of solid particles and liquid, which is surrounded by an outer porous shell of solid particles that grows in thickness because of the surface regression. Singular perturbation expansions were used to obtain approximate solutions for the temperature profiles of the inner sphere and the regression velocity of its surface. The expansion parameter is the ratio of energy required to raise the inner sphere to the liquid vaporization temperature, to that required for liquid vaporization, a type of Stefan number. For small values of the parameter it was shown that the inner sphere is heated by the inward diffusion of energy from the regressing surface. The cube of the diameter of the inner sphere then decreases linearly with time, to a first approximation. An approximate expression for the vaporization time is linearly proportional to both the liquid volume fraction and the square of the overall droplet diameter. For large values of the parameter it was shown that the inner sphere is heated by the inward propagation of a thermal wave front located at the regressing surface. An approximate expression for the vaporization time is derived and the square of the overall droplet diameter decreases linearly with time [41].

3. Experimental Work

The methods of analysis employed for large boron loadings also may be applied at low boron loading if the rigid-shell model is replaced by a contracting-sphere model [45,47]. It was then found that the square of the droplet diameter decreased linearly with time for both large and small Stefan numbers, but the slopes of the square laws differed in the two limits. The analysis also applies to a pure liquid droplet and for large Stefan numbers, gives a burning-rate constant that differs from the classical expression. This new result for liquid droplet burning, and the thermal-front physics associated with the new result, deserve to be tested further through pure-liquid droplet-combustion experiments. With slurries, the theory predicts that the contracting-sphere model may be applied until a rigid-porous-shell limit is reached, after which the rigid-shell model should be applied. An experimental program with suspended slurry droplets was undertaken to test these predictions.

a. Suspended Droplets

Single fiber-supported slurry droplets of boron in JP-10 were ignited and burned in room-temperature air [46,47]. Initial droplet diameter ranged from 1.2 to 3.0 mm and initial boron weight fractions f , from 0 to 0.7. It was observed that although the liquid fuel apparently burns completely, the boron does not ignite under these experimental conditions. For the pure liquid, the combustion was observed to be smooth, with a measured burning-rate constant of $0.143 \text{ mm}^2/\text{s}$. At low f there was found to be periodic swelling of the droplet with mildly disruptive emission of gas from the interior; the severity of this irregularity is greatest for $f > 0.1$ and negligible for $f > 0.2$. For $f > 0.4$ a reduction in droplet diameter according to a square law was observed for a period of time, followed by a burning period of essentially constant diameter. For $f > 0.5$, the droplet diameter remains practically constant during combustion, although the measured burning time conforms to a square law. These observations were compared quantitatively with the theoretical predictions discussed above and were found to agree within accuracies ranging from 10% to 25%. Thus, experimental support was obtained for the results of the theoretical analysis. The theoretical results, therefore, may be used to estimate temperature profiles within burning slurry droplets during the hydrocarbon-burning phase, as a first step toward an analysis for predicting possible conditions of disruption. The importance of addressing questions of disruption became apparent in the experimental research on full droplets of boron slurries.

b. Free Droplets

The experimental studies in burning of free slurry droplets have progressed substantially during this period.

Despite the considerable attention that boron slurries have received in recent years as potential high-energy density liquid fuels, very little fundamental work on the actual vaporization/combustion of isolated droplets has been reported to date. The primary purpose of the current work was to investigate the fundamental vaporization/combustion behavior of boron slurry droplets and to provide information useful for fuel and combustor development efforts. First observations were made on the combustion properties of isolated boron slurry droplets [42,44,48].

Initial observations of burning free droplets of boron/JP-10 slurry fuels were made in a high-temperature oxidizing environment under conditions of low Reynolds number. An array of well-dispersed droplets (spaced approximately 100 droplet diameters apart) was projected downward through the center of a premixed, water-cooled, flat-flame burner, coaxially into a hot post-combustion gas. A droplet generation system

utilizing an aerodynamic technique was specifically revised under the current period in order to produce small droplets (approximately 300 μ m dia.) of highly viscous slurry fuels at room temperature with substantially high solid particle loading (> 30 wt. %). The flat-flame burner producing the post-combustion gases was operated at atmospheric pressure using fuel-lean mixtures of methane, hydrogen, oxygen and nitrogen. This provided a hot oxidizing environment in the post-combustion gas which supported an envelope diffusion flame around the droplet. The equivalence ratio of the premixed flame gases was varied between 0.3 - 0.7 to vary the environmental oxygen content and the temperature of the post-flame gases. The relative velocity of the gas and the droplet was minimized to obtain the low Reynolds number conditions. Boron slurry fuels supplied by three different manufacturers (Sun Tech Co., Atlantic Research, UOP) were used and diluted with pure JP-10 fuel (exo-tetrahydrodicyclopentadiene) in order to produce identical particle loadings for each slurry (40%). These samples could then be diluted by addition of JP-10 to achieve any lesser particles loading desired. Some additional JP-10 slurries containing carbon-black or aluminum and are planned to be tested for composition under a new AFOSR contract.

Cinematographic and photographic observations of the burning free droplets, utilizing either direct flame luminescence or back-lighting, were made using both 16 mm high-speed cinematography and 35 mm single-lens reflex photography. A laser-triggered, stroboscopic back-lighting system was used for obtaining well-focused instantaneous pictures when taking single-lens reflex photographs. By splitting the laser beam into two parallel beams with a known separation distance (~ 2 mm), droplet flight time and hence droplet velocity was obtained by sensing the light scattered from the droplet passing through the laser beams. The injection velocities of droplets were typically between 2.5 - 3 m/s and resulted in an observation time of up to 400 ms.

Droplets of boron slurry, injected into the hot oxidizing environment, were ignited after a short period (5 - 10 ms) and diffusion flames of the vaporization liquid component were developed around the droplets. Yellow luminosity due to soot particles in the diffusion flame was observed as is similar to pure hydrocarbon droplet flames. After a period of quiescent combustion (50 - 100 ms), violent disruption of the slurry droplets and subsequent ignition and rapid burning of the solid component (boron) were observed. The disruption and boron combustion resulted in a bright greenish flash and a popping sound. This disruption may be attributable to entrapment of the liquid component in the slurry droplet interior and subsequent superheating and nucleation. As a result of the disruption, the size of agglomerates of the solid component formed during liquid vaporization is significantly reduced. These observations are

quite different than those hypothesized by several investigators previously who suggested that slurry combustion might be primarily influenced by the formation of (dry) agglomerates containing essentially all of the solids within the initially injected drop. Apparently, substantial liquid remains in the concentrated solids when disruption occurs. Due to this second atomization of boron slurry drops, the combustion rate of solids is substantially enhanced over that of such large (dry) agglomerates and difficulties in designing compact combustors may not be as severe as initially hypothesized. More importantly, the initiation of disruption appears to be characteristic of all slurries currently produced by various manufacturers and may not require substantial quantities of additional additives specifically designed for such purposes.

This work fully substantiates the occurrence of disruption in the combustion of boron slurry droplets, but it does not fully identify the range of parameters over which disruption occurs (e.g. particle loading, additive type, effect of droplet Reynolds number, effect of pressure, etc.), nor the mechanism which produce disruption. These open questions remain and are being considered in the follow-on investigations under the new AFOSR contract.

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(All are program contributions except 23, 24, 26, 27, 28, 31, 32, 37, 39 and 43).

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CHEMICAL KINETIC FLOW REACTOR

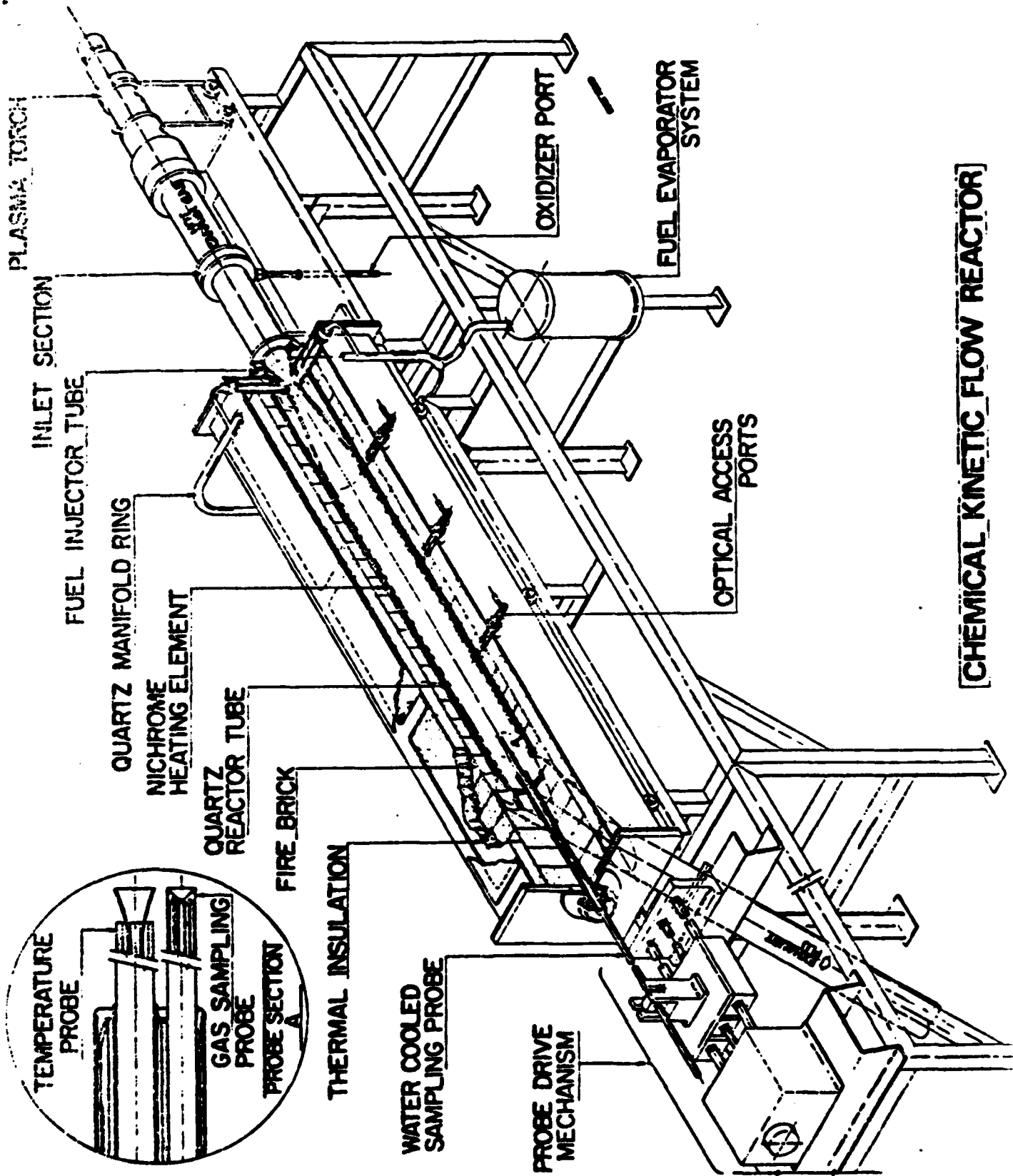


Figure 1

n-PROPYLBENZENE OXIDATION - $PHI=1.5$, $T=1003K$

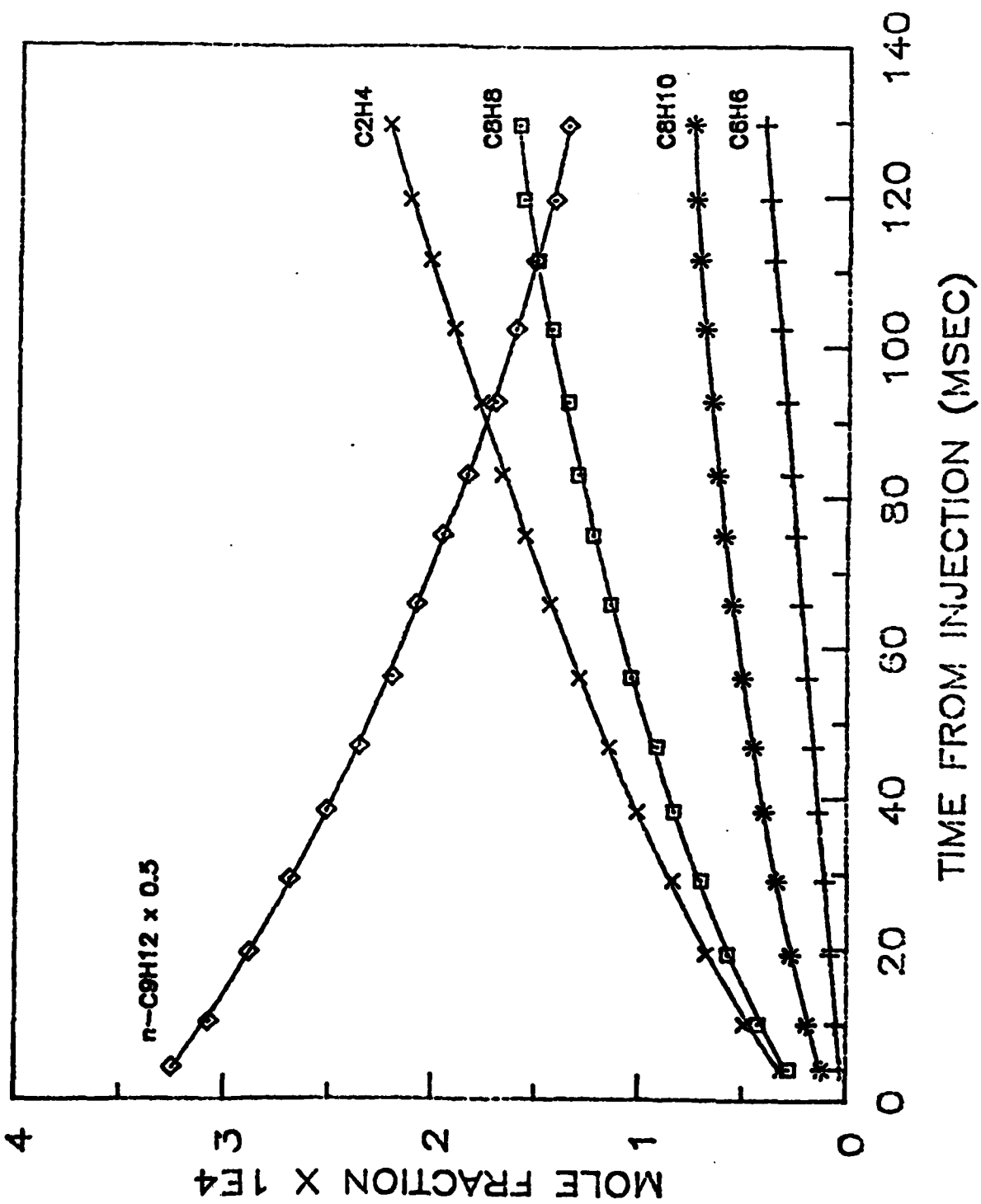


Figure 2

ISOPROPYLBENZENE OXIDATION - $\text{PHI}=1.5$, $T=1003\text{K}$

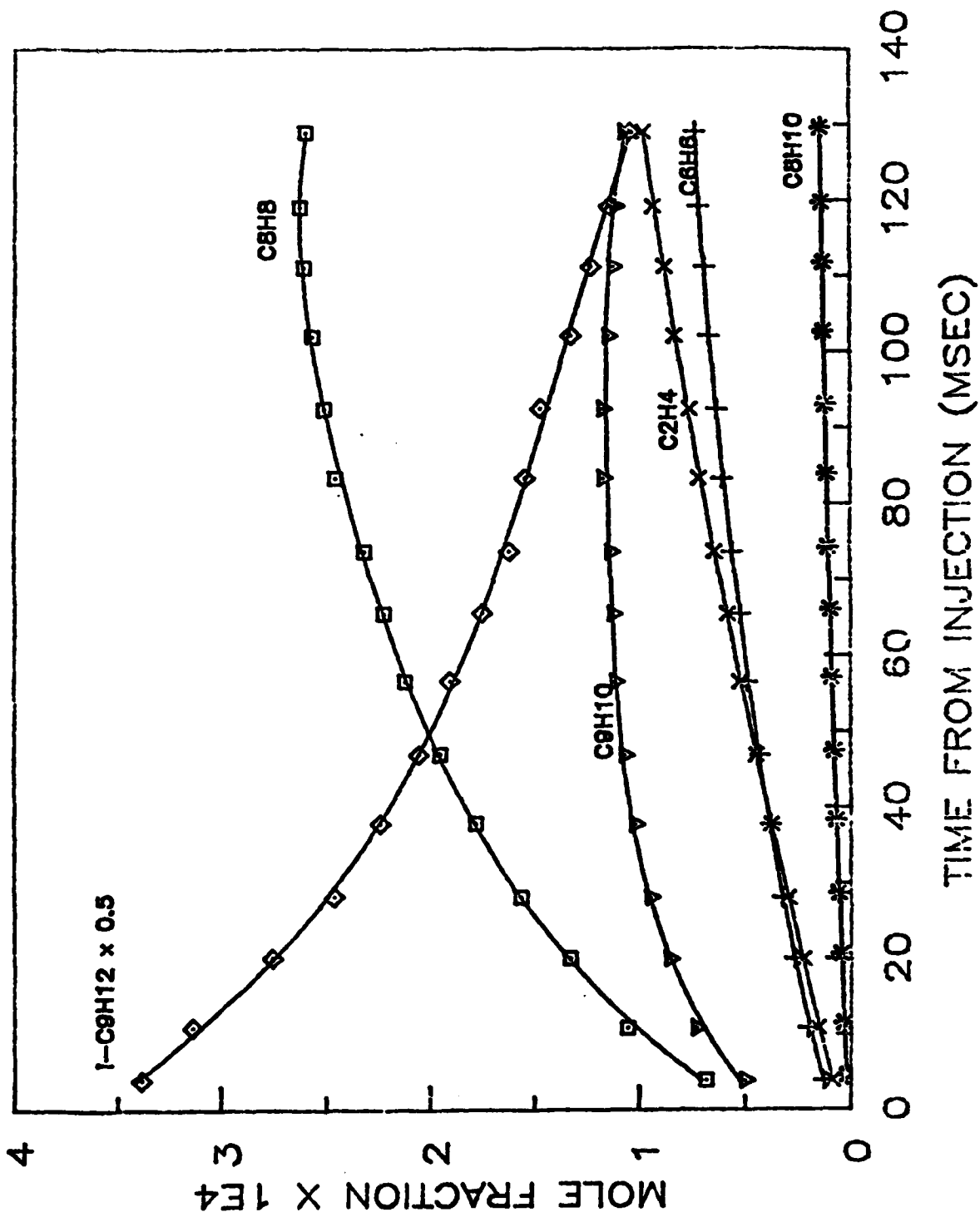


Figure 3

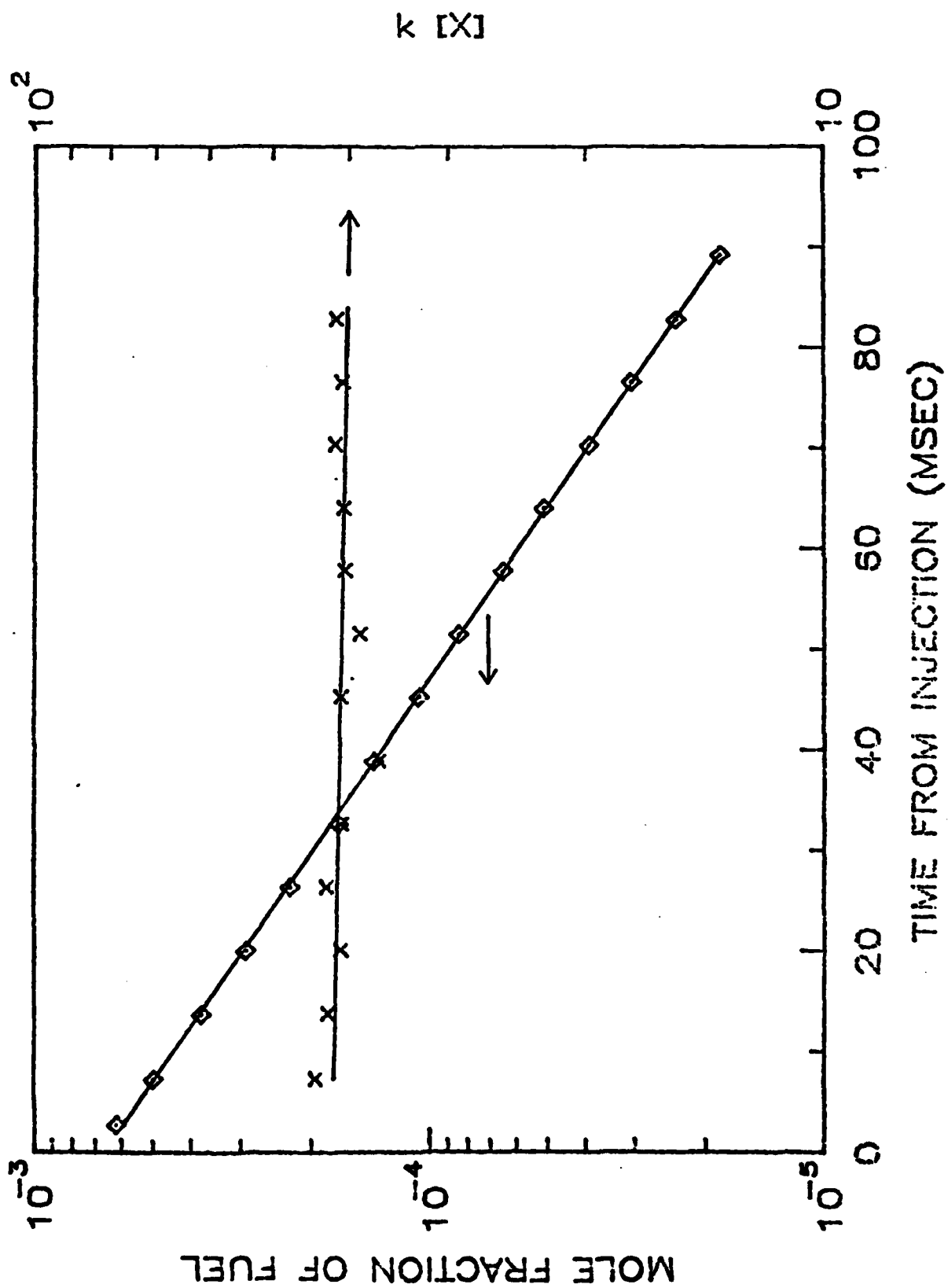


Figure 4

STYRENE OXIDATION — $PHI=0.56$

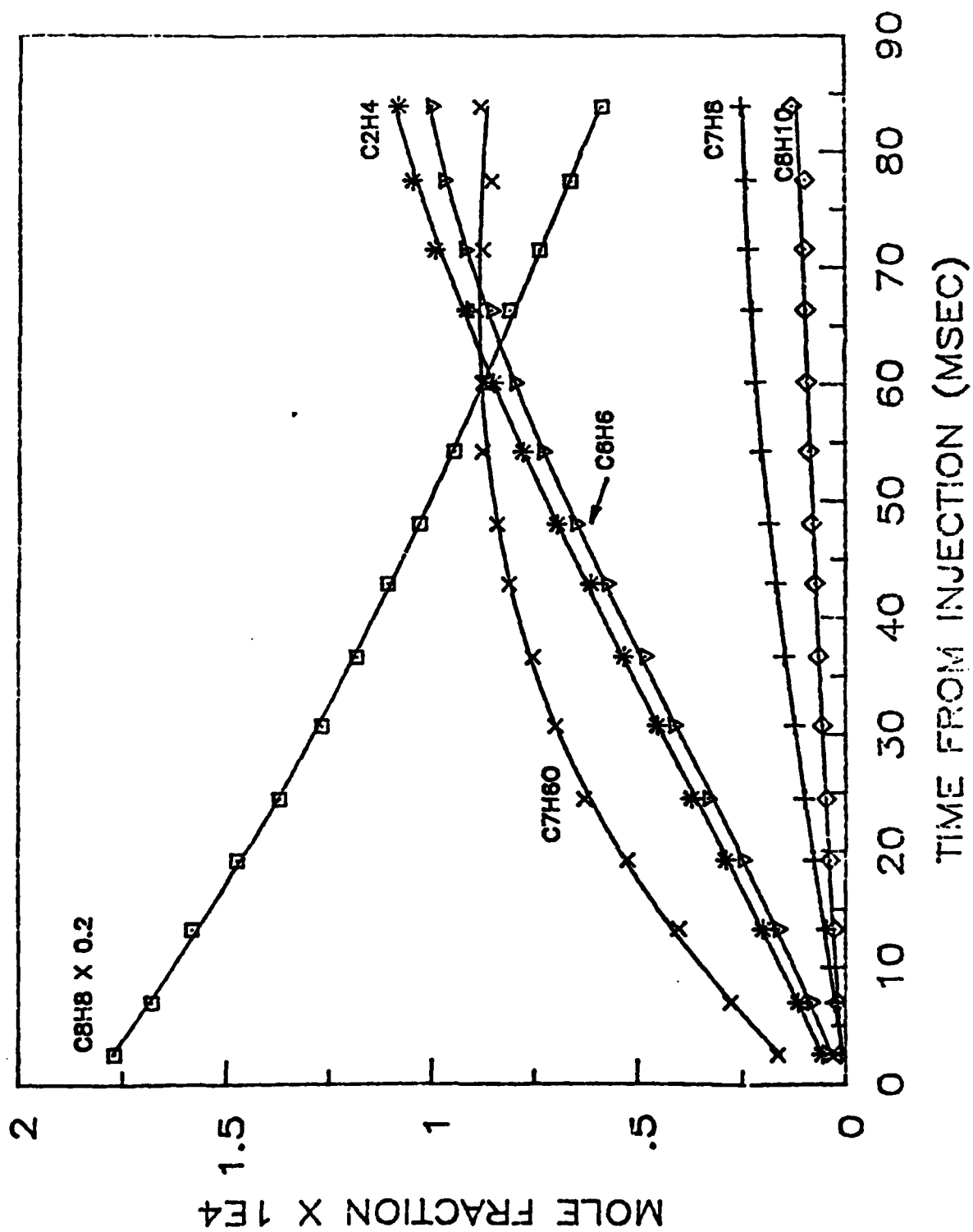


Figure 5

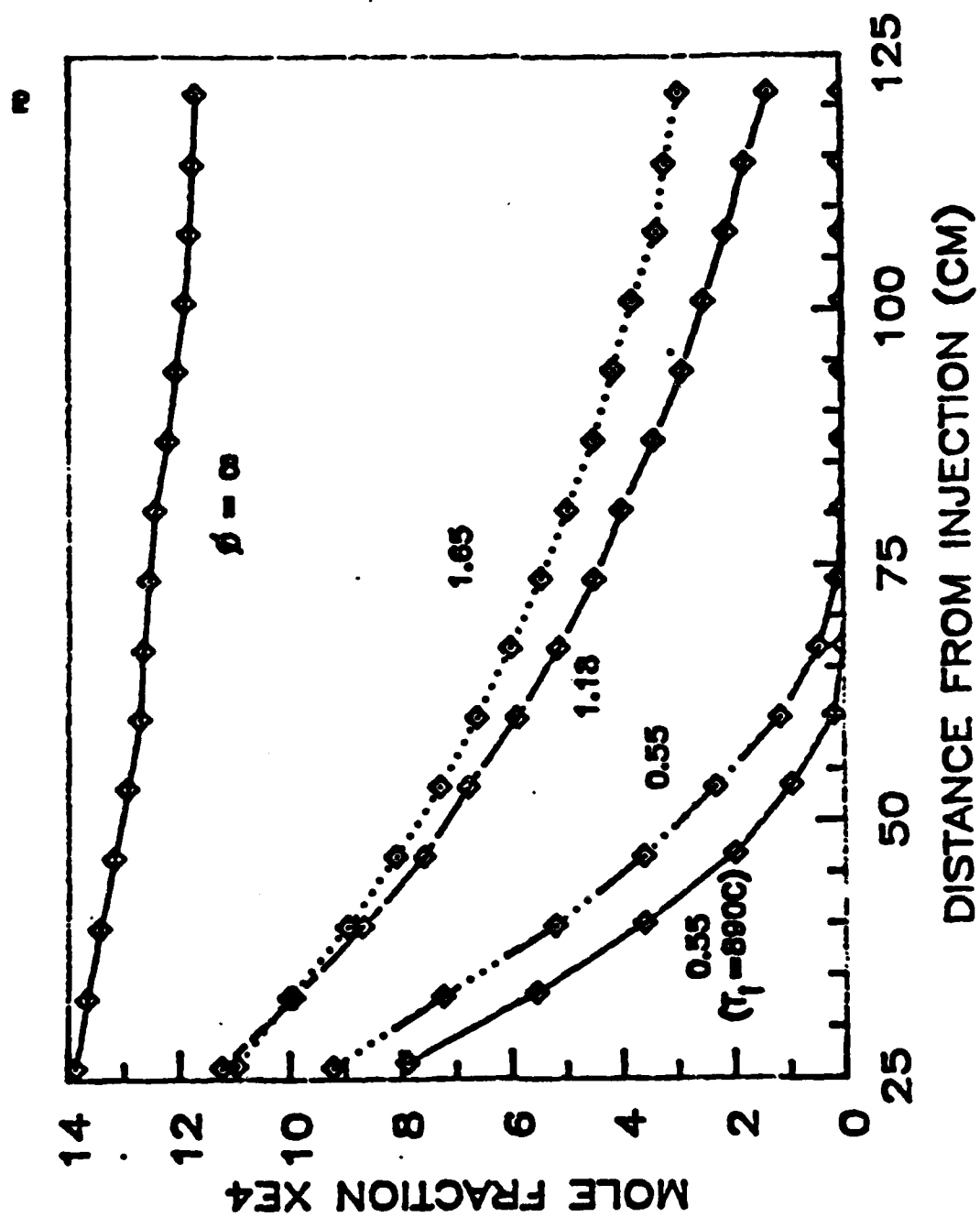


Figure 6

BENZENE/1-HEXENE MIXTURES

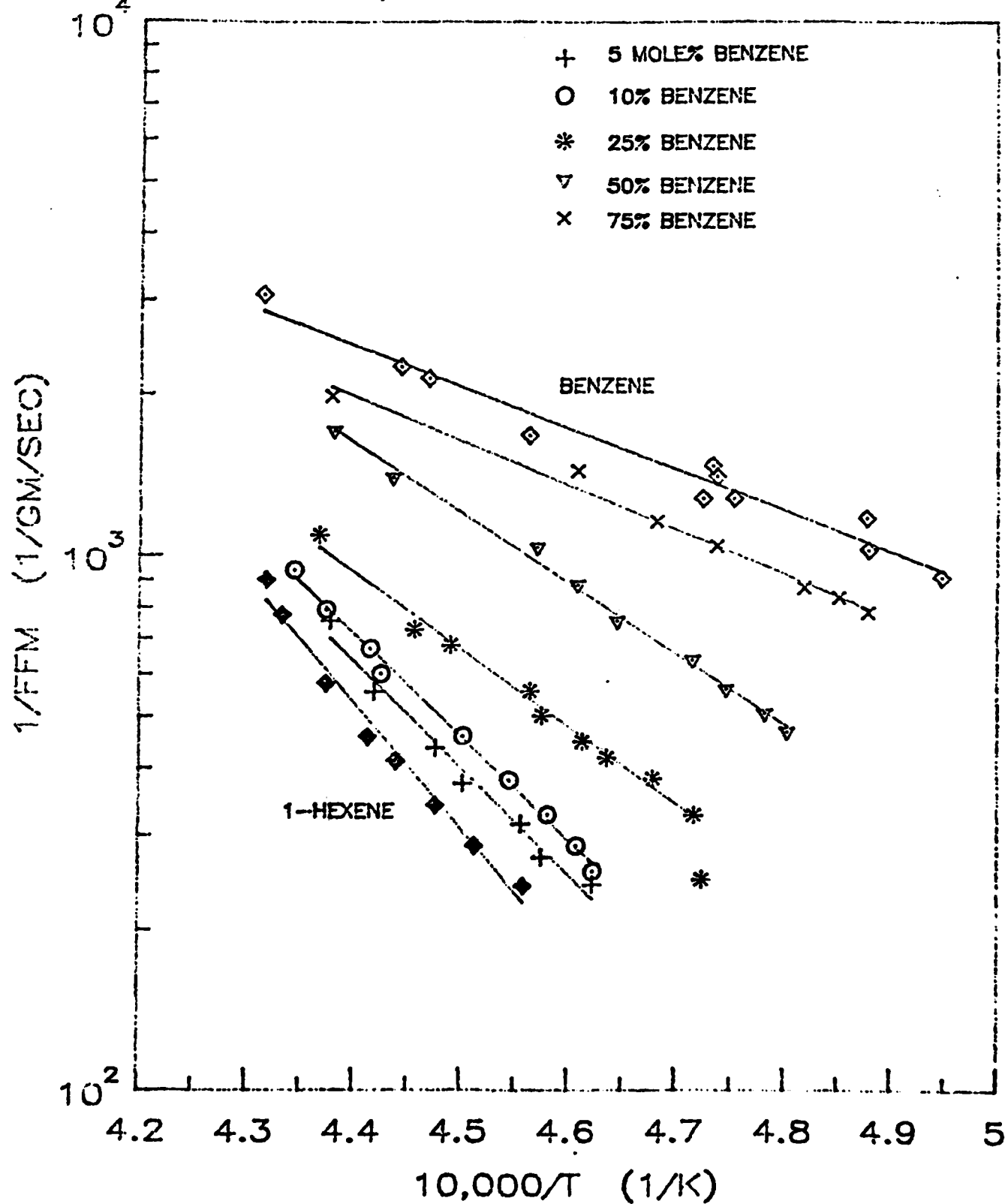


Figure 7

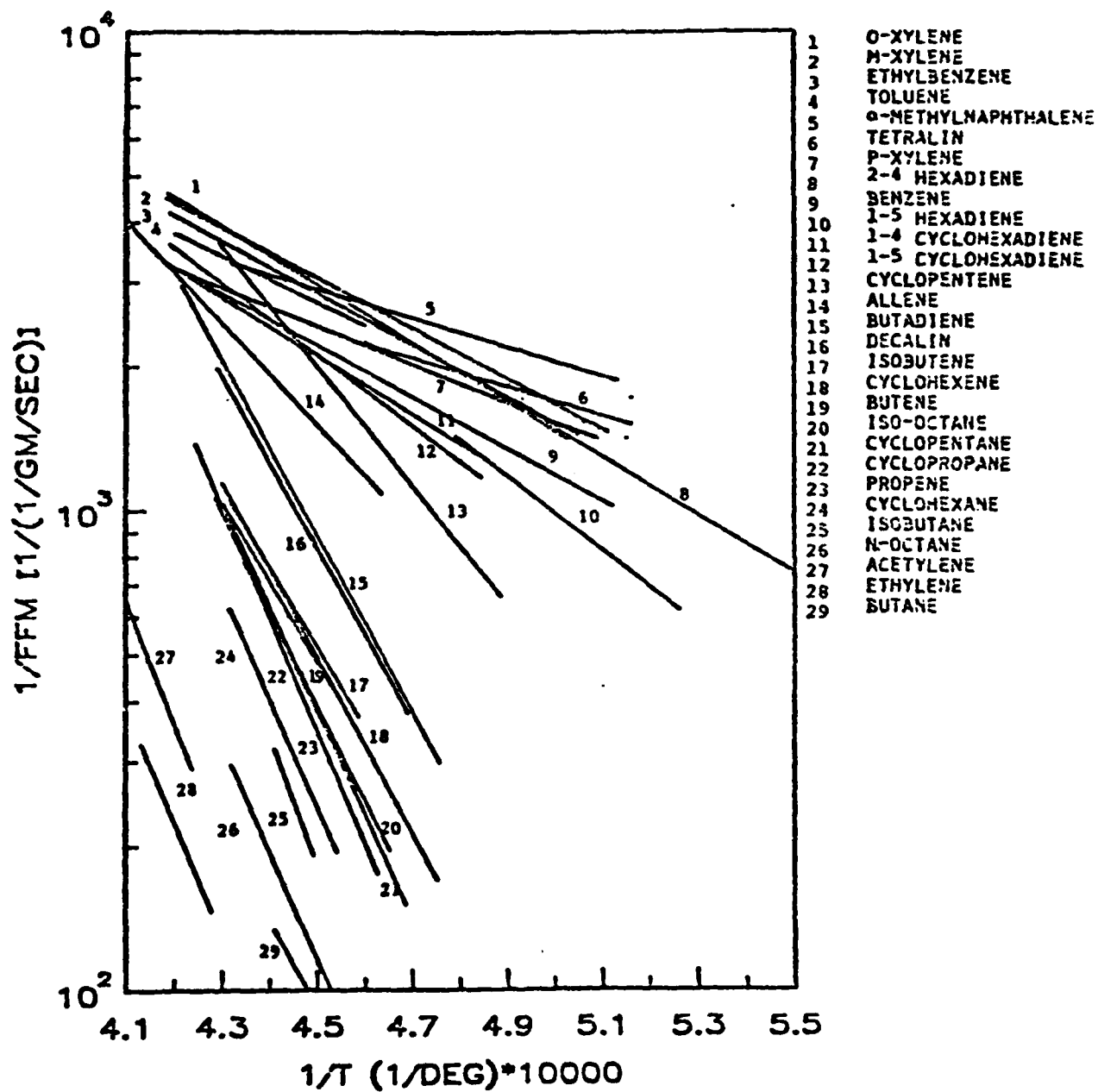


Figure 8

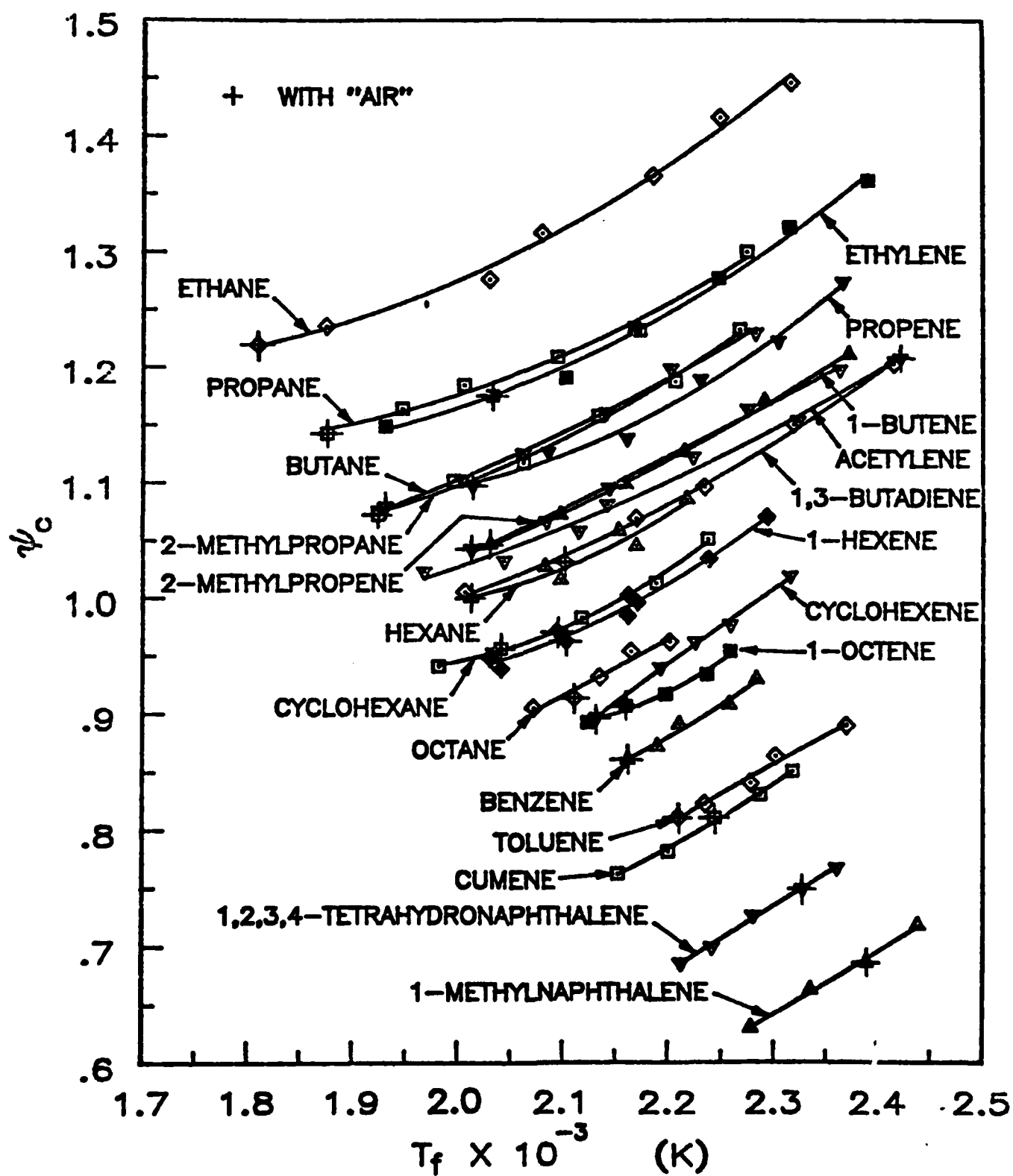


Figure 9

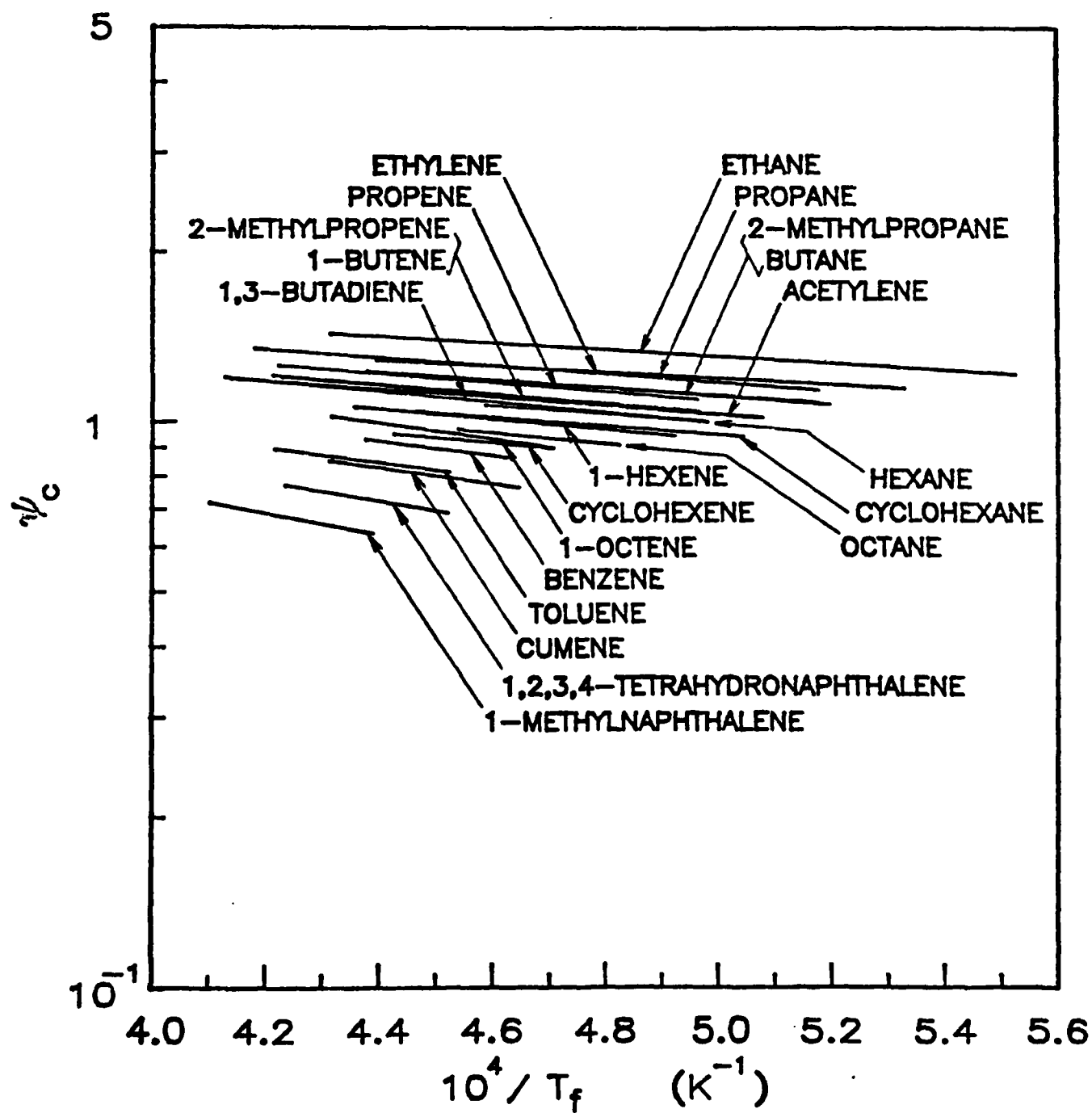


Figure 10

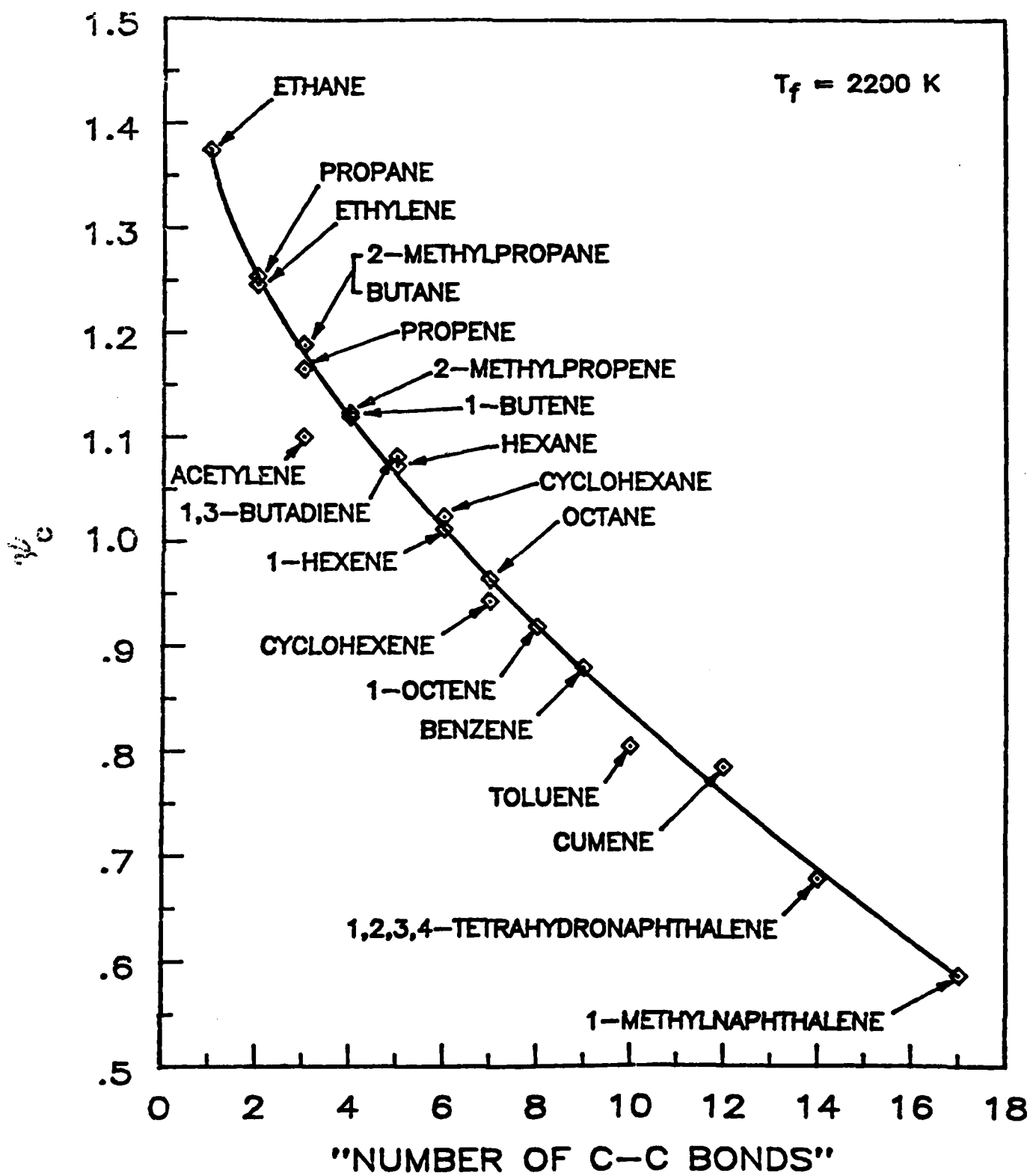


Figure 11

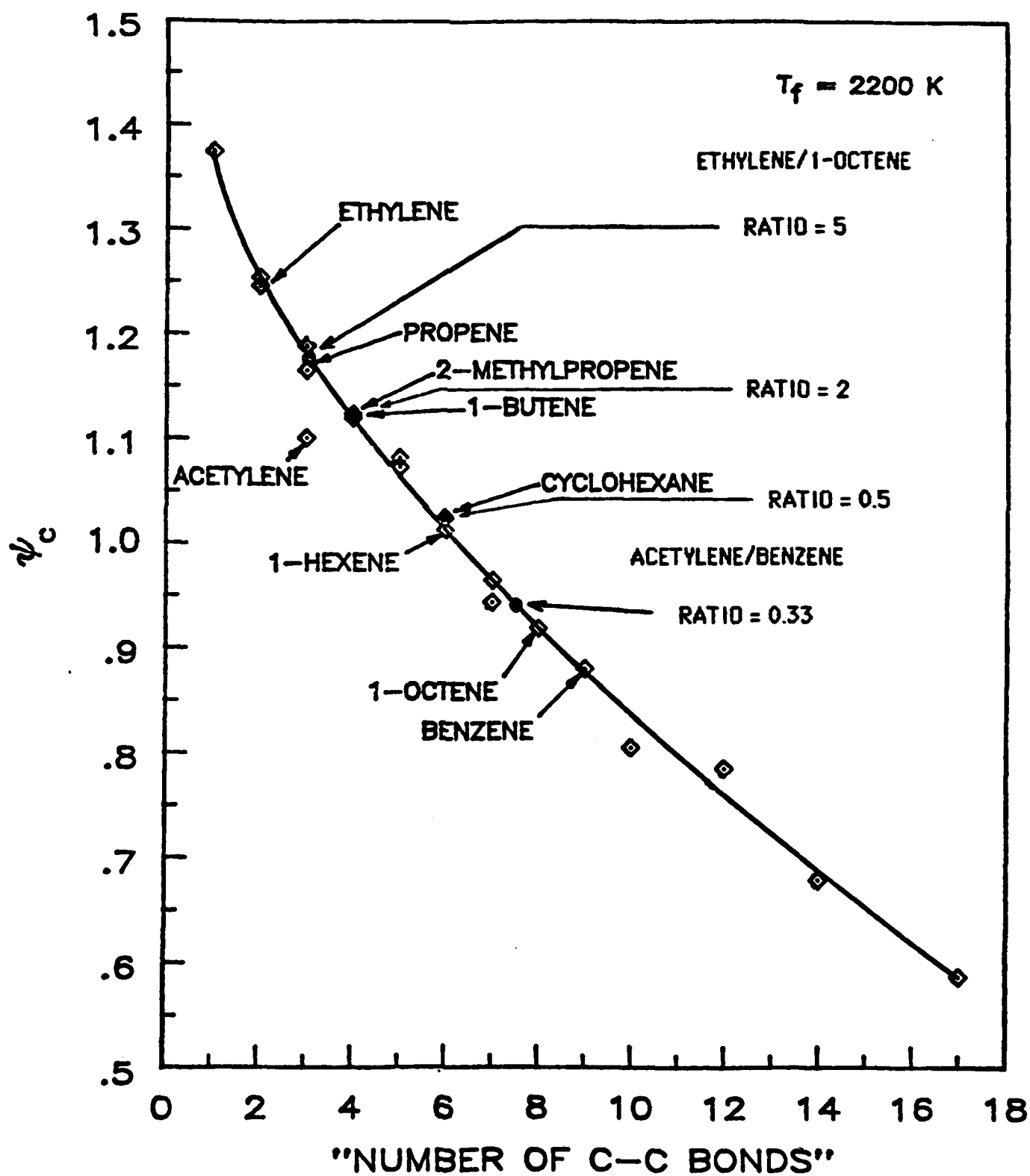


Figure 12

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